EFFECT OF VARIOUS ADDITIVES ON THE PROPERTIES OF POLY(L-LACTIC ACID)/POLY(BUTYLENE SUCCINATE-CO-L-LACTATE) BLEND

by

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LIST OF SYMBOLS

α	Alpha-form crystal structure
β	Beta-form crystal structure
θ	Diffraction angle
d	Spacing between the diffraction plane
I	Intensity of the X-Ray peak
$tan\ \delta$	Loss factor
E	Modulus of elasticity
E'	Storage modulus
E''	Loss modulus
T_g	Glass transition temperature
T_c	Crystallization temperature
T_m	Melting temperature
X_c	Degree of crystallinity
ΔH_c	Enthalpy of crystallization
ΔH_m	Enthalpy of melting
ΔH°_m	Enthalpy of fusion
x	Weight fraction of PLLA
$T_{50\%}$	Decomposition temperature at 50% of weight loss
K_{IC}	Fracture toughness
P	Maximum load
S	Span length
a	Notch length
σ_f	Flexural stress

ε_f	Flexural strain
t	Thickness of specimen
b	Width of specimen
w_o	Original weight of the specimen
w_w	Wet weight of the specimen
w_d	Dry weight of the specimen

LIST OF ABBREVIATIONS

ASTM	American Standard Test methods
CNT	Carbon nanotube
DTG	Derivative Thermogravimetry
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
PBSL	Poly(butylene succinate-co-L-lactate)
PEA	Poly(ethylene adipate)
PLLA	Poly(L-lactic acid)
PTMEG	Poly(tetramethylene ether glycol)
SBF	Simulated body fluid
SENB	Single edge notch bending
TGA	Thermogravimetric Analysis
TiO_2	Titanium dioxide
XRD	X-Ray Diffraction

KESAN PELBAGAI PENAMBAH KE ATAS SIFAT-SIFAT ADUNAN POLI(L-LAKTIK ASID)/POLI(BUTILENA SUKSINAT-KO-L-LAKTAT)

ABSTRAK

Adunan polimer poli(L-laktik asid) (PLLA)/poli(butilena suksinat-ko-L-laktat) (PBSL) pada pelbagai nisbah pengadunan telah disediakan melalui kaedah pencampuran lebur. Pengadunan PLLA dengan PBSL meningkatkan keliatan dan kestabilan terma bagi adunan PLLA. Namun begitu, kekuatan dan modulus lenturan menurun dengan penambahan kandungan PBSL. Penyepuhlindapan dijalankan selepas nisbah pengadunan yang optima dikenalpasti. Analisis terhadap masa penyepuhlindapan menunjukkan bahawa tahap pengkristalan dan modulus lenturan meningkat dengan peningkatan dalam masa penyepuhlindapan. Seterusnya, poli(etilena adipat) (PEA) dan poli(tetrametilena eter glikol) (PTMEG) telah ditambah sebagai penserasi dalam adunan PLLA/PBSL tersebut. Analisis FTIR menunjukkan bahawa interaksi secara fizikal di antara PEA dan PLLA/PBSL berlaku dan ini adalah disebabkan oleh daya sekunder. Kekuatan lenturan menunjukkan pergantungan terhadap interaksi daya sekunder di antara PEA dan PTMEG dengan adunan tersebut. Kesan adunan PLLA/PBSL dengan pelbagai kandungan titanium dioksida (TiO_2) dan karbon tiub bersaiz nano (CNT) telah dikaji. Peningkatan modulus lenturan sebanyak 4.3% dan 8.4% masing-masing didapati dengan penambahan 0.25 phr TiO_2 dan CNT. Lapisan apatit terhasil pada permukaan komposit yang mengandungi TiO_2 tiub bersaiz nano selepas perendaman dalam cecair tubuh tersimulasi selama tujuh hari. Peningkatan dalam penyerapan air bagi komposit nano PLLA/PBSL/TiO_2 berlaku dengan peningkatan dalam kuantiti pengisi. Komposit nano PLLA/PBSL/CNT menunjukkan kecenderungan penyerapan air yang mirip dengan adunan PLLA/PBSL.

EFFECT OF VARIOUS ADDITIVES ON THE PROPERTIES OF POLY(L-LACTIC ACID)/POLY(BUTYLENE SUCCINATE-CO-L-LACTATE) BLEND

ABSTRACT

Polymer blends of poly(L-lactic acid) (PLLA) and poly(butylene succinate-co-L-lactate) (PBSL) at various blending ratios were prepared through melt mixing method. The blending of PLLA with PBSL resulted in an improvement in the toughness and thermal stability of the PLLA blend. However, flexural strength and modulus decreased with the increase in PBSL content. Annealing was conducted after the optimum blending ratio was determined. Analysis on the annealing revealed that the degree of crystallinity and flexural modulus were enhanced with increasing annealing time. Next, poly(ethylene adipate) (PEA) and poly(tetramethylene ether glycol) (PTMEG) were added as compatibilizers to the PLLA/PBSL blend. The FTIR analysis showed that the physical interaction between PEA and PLLA/PBSL blend occurred and this was due to the presence of secondary force. The flexural strength exhibited a dependency on the extent of the secondary force interaction between PEA and PTMEG with the blends. The effect of PLLA/PBSL blend with varying contents of titanium dioxide (TiO_2) and carbon nanotubes (CNT) were investigated. An increase in flexural modulus of 4.3% and 8.4% was obtained with the addition of 0.25 phr TiO_2 and CNT, respectively. Apatite layer was formed on the surface of the nanocomposite containing TiO_2 nanotubes after soaking in simulated body fluid (SBF) for 7 days. An increase in the water absorption of the PLLA/PBSL/TiO_2 nanocomposite occurred with increased filler loading. The PLLA/PBSL/CNT nanocomposite exhibited an increasing trend of water absorption similar to the PLLA/PBSL blend.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Today, public concern about the environment, climate change and limited fossil fuel resources are important drivers for governments, companies and scientists to find alternatives to crude oil. Petroleum-based plastics are increasingly polluting the sea, with the most prominent example being the so-called Great Pacific Garbage Patch in the central North Pacific Ocean (Moore, 2001). In addition, the rising amounts of waste and limited landfill capacities are mainly caused by the non-degradable polymers. Therefore, bio-based polymers that are derived from various natural botanical resources have been regarded as substitutes for petrochemical based plastics because they are abundant, renewable, and biodegradable. They may offer important contributions by reducing the dependence on fossil fuels and the related environmental impacts.

1.2 Problem Statement

Being biodegradable and biocompatible, poly(L-lactic acid) (PLLA) becomes one of the promising materials used as bone fixation devices in orthopedics (Sawalha et al, 2008). However, its high brittleness, low thermal stability and non-bioactivity have restricted its applications.

In this context, modification of PLLA is vital for properties enhancement. It can be done by blending with ductile biodegradable polymers such as poly(ε-caprolactone) (PCL) (Aslan et al., 2000), poly(butylene succinate) (PBS) (Shibata et

al., 2006), and poly(hydroxyl ester ether) (Cao et al., 2003). To the author's knowledge, there have been only a few investigations regarding the PLLA/PBSL blend. Thus, PBSL was selected for blending with PLLA in this study.

In general, the crystallization behavior of semicrystalline polymers has vital effects on their physical, mechanical, and thermal properties. The crystalline structure of a semicrystalline polymer, such as PLLA, has been shown to greatly depend on its thermal history and pretreatment (Shay and Caruther, 1990). Hence, annealing process was conducted on the prepared PLLA/PBSL blend to investigate the effect of annealing time on the mechanical and thermal properties of the samples.

Nevertheless, the PLLA/PBSL blend is immiscible, and the poor interfacial adhesion between the two phases reduces the flexural strength and fracture toughness of the blend. Its miscibility can be improved by using a compatibilizer of similar chemical structure to the constituting polymers of the blend to form a good interaction, either physically or chemically, between both polymers in the blend (Heino et al., 1997; Horak et al., 2002). The role of secondary forces in enhancing the miscibility of polymer blends has been clearly documented by Shafee (2002) and Kim and Kim (2006). In the present work, poly(ethylene adipate) (PEA) and polytetramethylene ether glycol (PTMEG) were used as compatibilizers for the PLLA/PBSL blend to modify the immiscible morphology and mechanical properties of the PLLA/PBSL blend. No study on the compatibilization of the PLLA/PBSL blend with these two materials has been reported yet. Both PEA and PTMEG contain hydroxyl groups at both ends of the molecules. It is believed that these hydroxyl terminal groups (-OH) might interact with the carbonyl group of PLLA and PBSL through transesterification. Furthermore, the presence of carbonyl groups (C=O) from PEA might create polar interaction with carbonyl groups of PLLA and PBSL.

Besides that, the issues of high material cost, low moisture stability, and non-bioactivity of PLLA can be solved through the addition of reinforcements. In recent years, bioactive materials are being widely used in biomedical applications due to their ability to elicit a specific biological response at their interface with a living tissue, which results in the formation of a bond between the tissue and the material. In this study, titanium dioxide (TiO_2) and carbon nanotube (CNT) were used as fillers for PLLA/PBSL blend. Viitala et al. (2001) and Uchida et al. (2003) reported that TiO_2 could form a bioactive apatite layer on the implant surface, which leads to new bone formation. On the other hand, CNT with diameter less than 100 nm was able to increase the osteoblast proliferation without showing any cytotoxicity (Elias et al., 2002). Both of the materials exhibited potential for use in orthopedic applications (Boyan et al., 1996).

Therefore, PLLA/PBSL blends containing different types of compatibilizers and nanofillers were developed. The effects of the additives contents on the mechanical properties, thermal properties, and *in vitro* bioactivity of the blend system were investigated in this study.

1.3 Objectives

The objectives of this study are listed as follows:-

(i) To determine the optimum blending ratio of PLLA/PBSL blend system.

(ii) To investigate the effect of annealing time on the mechanical and thermal properties of PLLA/PBSL blend.

(iii) To compare the effect of two different types of compatibilizers on the mechanical and thermal properties of PLLA/PBSL blend.

(iv) To study the effect of incorporation of nanofillers on the mechanical properties, thermal properties and *in vitro* bioactivity of PLLA/PBSL blend.

1.4 Outline of Dissertation

The present research work is aiming to improve the mechanical properties, thermal properties, and bioactivity of poly(L-lactic acid) by adding different additives to it.

The Problem statement, objectives of the study and the dissertation overview are presented in Chapter 1.

Chapter 2 comprises of the literature review on biodegradable polymers, polymer blends, nanocomposites, and the applications of PLLA.

In Chapter 3, specifications of the raw materials, research methodology, and the characterizations employed in this work are described.

The results of characterizations, and the discussions on the effect of annealing, compatibilizers and nanofillers on the properties of PLLA/PBSL blend are presented in Chapter 4.

Chapter 5 summarizes the conclusion of the study as well as several suggestions and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Biodegradable Polymers

The American Society for Testing of Materials (ASTM) defines biodegradable polymers as those which undergo a significant change in chemical structure under specific environmental conditions (Kolybaba et al., 2003). These changes result in a loss of physical and mechanical properties, as measured by standard methods. Biodegradable polymers undergo degradation from successive chemical reactions, such as hydrolysis and oxidation with or without the aid of enzymes in living organisms depending on the environmental conditions.

In general, biodegradable polymers are categorized into two groups according to their origin, namely natural biodegradable polymers, and synthetic biodegradable polymers (Smith, 2005). Natural biodegradable polymers are those that are produced from natural resources. There are six sub-classes of natural biopolymers, namely polysaccharides, proteins, lipids, polyesters formed by micro-organism, polyesters synthesized from bio-derived monomers, and miscellaneous polymers. The examples of each sub-class are summarized in Table 2.1.

Table 2.1 Overview of sub-classes of natural biodegradable polymers (Smith, 2005).

Sub-class	Examples	Sources
Polysaccharides	Starch	Corns & potatos
	Cellulose	Wood & stalks of sugarcane bagasse
	Lignin	Wood pulps & sugarcane waste
	Chitin	Shells of crabs, lobsters, shrimps & insects
Proteins	Collagen	Animals
	Soy protein	Soybeans
	Gluten	Wheats & corns
	Casein	Cow milk
Lipids	Fatty acid	Plant oils & animal fat
	Wax	
Polyesters formed by micro-organism	Polyhydroxyalkanoate (PHA)	*Bacillus subtilis* bacteria
	Polyhydroxybutyrate (PHB)	*Ralstonia eutrophus* bacteria
Polyesters synthesized from bio-derived monomers	Polylactic acid (PLA)	Beet sugar, potato & corn strach
Miscellaneous polymers	Natural rubbers	Latex produced by some plants such as *Para* rubber trees

On the other hand, synthetic biodegradable polymers are synthesized from crude oil. These polymers are classified into four groups, namely aliphatic polyesters, aromatic polyesters, polyvinyls, and modified polyolefins. Table 2.2 shows the overview of synthetic biodegradable polymers.

Table 2.2 Overview of sub-classes of synthetic biodegradable polymers (Smith, 2005).

Sub-class	Examples	Production method
Aliphatic polyesters	Poly(glycolic acid) (PGA)	Ring opening of glycolide, a diester of glycolic acid
	Poly(lactic acid) (PLA)	Ring opening of lactide, a diester of lactic acid
	Poly(butylene succinate) (PBS)	Polycondensation of glycols and dicarboxylic acids
	Poly(ε-caprolactones) (PCL)	Ring opening polymerization of ε-caprolactone
Aromatic polyesters	Poly(ethylene terephthalate) (PET)	Polycondensation of aliphatic glycols and terephathalic acid
	Poly(butylene terephthalate) (PBT)	
Polyvinyls	Poly(vinyl acetate) (PVAc)	Free radical polymerization of vinyl acetate
	Poly(vinyl alcohol) (PVA)	Hydrolysis of polyvinyl acetate
	Poly(vinyl chloride) (PVC)	Free radical polymerization of the monomer vinyl chloride
Modified polyolefins	Poly(ethylene) (PE) with specific agents sensitive to light or temperature, such as Oxo-Biodegradable Film	Free radical, anionic or cationic polymerization of ethylene monomer

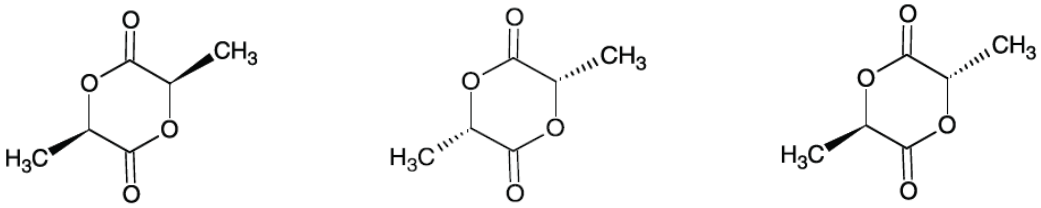
Since this research work is focusing on poly(L-lactic acid) (PLLA) and poly(butylene succinate-co-L-lactate) (PBSL), aliphatic polyesters will be described in details in the next sections.

2.2 Aliphatic Polyesters

Aliphatic polyesters have played a prominent role in the development of biodegradable polymers. Besides the natural polyesters, a number of synthetic aliphatic polyesters have been shown to be biodegradable. This family of biodegradable polymers is produced mainly through condensation polymerization of aliphatic dicarboxylic acids with diols, transesterification reaction of diesters with diols, polymerization of hydroxy acids, and ring-opening polymerization of lactones (Odian, 2004). They can be processed into various forms, such as fibers, films, and injection-molded devices (Gross and Kalra, 2002). They are suitable to replace many conventional thermoplastics because of their good mechanical strength and variable melting temperatures. Among them, poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) are the most famous aliphatic polyesters that are shown to be biodegradable. In the following section, the origin as well as the typical properties of these two important aliphatic polyesters will be described in details.

2.2.1 Poly(lactic acid)

Poly(lactic acid) (PLA) is one of the most important aliphatic polyesters commonly produced from α-hydroxy acids. Due to the chiral nature of lactic acid, PLA exits in three isomeric forms, namely, D(-), L(+) and racemic (D,L), as illustrated in Figure 2.1. Poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) are semi-crystalline solids having hydrolytic degradation rates similar to poly(glycolic acid) (PGA) (Johnson et al., 2003).



(a) D-lactic acid (b) L-lactic acid (c) D,L-lactic acid

Figure 2.1 The chemical structure of different stereoforms of lactic acid monomers; (a) D-lactic acid, (b) L-lactic acid, and (c) D,L-lactic acid (Johnson, 2003).

Lactic acid can be manufactured either by carbohydrate fermentation or chemical synthesis (Benninga, 1990). The majority of the world's commercially manufactured lactic acid is made by bacterial fermentation of carbohydrates, using homolactic organisms such as *Lactobacillus*, which exclusively forms lactic acid (Hartmann, 1998). Generally, most of the simple sugars obtained from agricultural byproducts can be used. These sugars include glucose, maltose, and dextrose from potato or corn starch; sucrose from cane or beet sugar; and lactose from cheese whey (Benninga, 1990). Nevertheless, the lactic acid produced from fermentation cannot be polymerized directly to a useful poly(lactic acid) because each polymerization reaction generates one molecule of water, which degrades the forming polymer chain to very low molecular weights. Instead, two lactic acid molecules undergo a single esterfication and then catalytically cyclized to make a cyclic dilactate ester. Although dimerization also generates water, it can be separated prior to polymerization due to a significant drop in polarity. PLA of high molecular weight is produced from the dilactate ester by ring-opening polymerization using stannous octoate as a catalyst (Garlotta, 2001). Figure 2.2 shows the ring opening polymerization of poly(lactic acid) derived from the microbial fermentation of glucose.

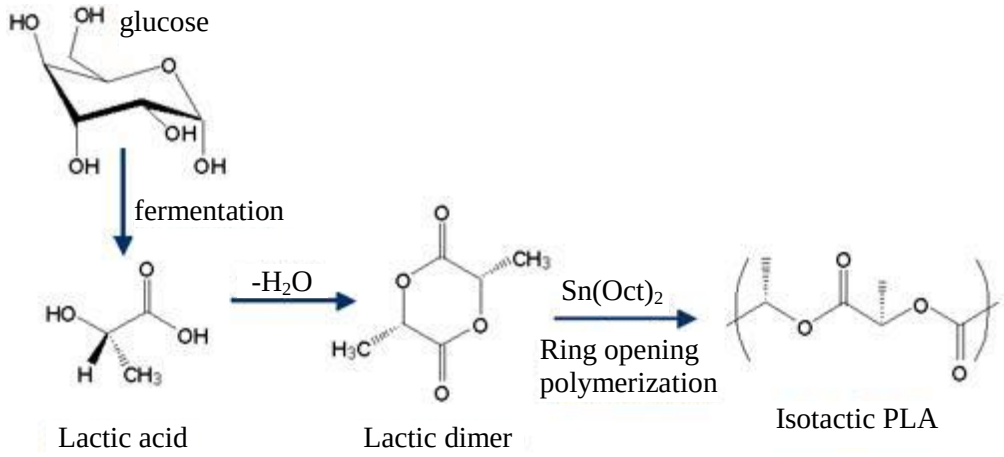


Figure 2.2 Ring opening polymerization of poly(lactic acid) derived from the microbial fermentation of glucose (Dorgan et al., 2001).

Besides that, lactic acid can also be synthesized by using petroleum-based chemicals. The synthesis of PLA from lactide ring, which is the cyclic dimer of lactic acid, is presented in Figure 2.3.

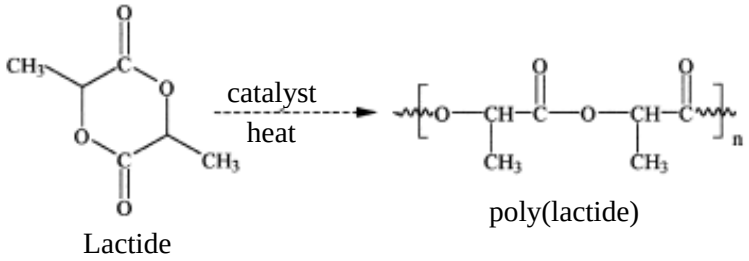


Figure 2.3 Synthesis of poly(lactide) (Middleton & Tipton, 2000).

Poly(lactic acid) has molecular weight (Mw) ranging from 5×10^4 to 50×10^4, with a polydispersity ranging from 1.8 to 2.6 (Suyatma et al. 2004). High molecular weight PLA is a reasonably transparent, glossy, stiff thermoplastic having mechanical properties comparable to commodity polymer such as poly(styrene) (PS). The tensile strength and modulus of elasticity of PLA are about 45 MPa and 3 GPa, respectively. However, PLA is a brittle polymer with elongation at break of about 4%

only. It can be processed by extrusion, thermoforming, fibre spinning, blow moulding or injection moulding. Poly(L-lactic acid) (PLLA) is more commonly used compared to poly(D-lactic acid) (PDLA) because the degradation product L-lactic acid is naturally occurring whereas D-lactic acid is synthetic (Smith, 2005). PLLA is about 37% crystalline with a glass transition temperature of 55 °C to 60 °C and a melting point of 175 °C to 180 °C. The crystalline PLLA is soluble in chlorinated solvents and benzene at elevated temperatures, whereas the amorphous PDLA is soluble in most organic solvents such as tetrahydrofuran (THF), chlorinated solvents, benzene, acetonitrile, and dioxane (Hartmann, 1998). PLLA is a non-toxic biodegradable polymer which can be readily degraded by hydrolysis under mild conditions to lactic acid, which is a common biodegradable organic acid naturally present in the human body. The degradation time of PLLA is between 18 and 24 months, depending on its degree of crystallinity. Furthermore, it is approved for human use by the US Food and Drug Administration. Therefore, PLLA becomes the most important plastic derived from renewable resources (Torres et al., 1996).

2.2.2 Poly(butylene succinate)

Poly(butylene succinate) (PBS) ($[-O(CH_2)_4OOC(CH_2)_2CO-]_n$) is an important member of the aliphatic polyester family. It is synthesized from succinic acid and 1,4-butanediol through polycondensation process (Takiyama & Fujimaki, 1994). The synthesis of PBS is illustrated in Figure 2.4.

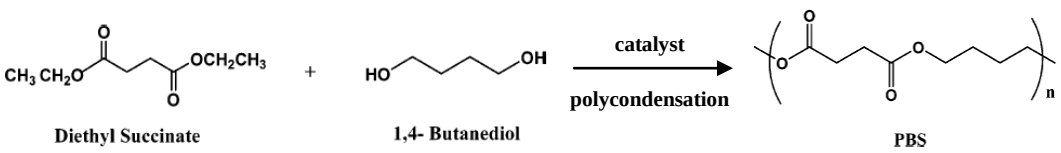


Figure 2.4 Synthesis of poly(butylene succinate) (Takiyama & Fujimaki, 1994).

PBS is a semicrystalline polymer having molecular weights ranging between 3×10^4 and 20×10^4 with a wide polydispersity ranging from 2.0 to 6.3 (Jin et al., 2000). Its mechanical properties such as tensile strength and flexibility, its transparency and biodegradability depend on the crystal structures and the degree of crystallinity to some extent. PBS is a flexible polymer having mechanical properties comparable to polypropylene (PP) and low-density polyethylene (LDPE). It possesses a tensile strength of about 28 MPa and elongation at break of about 100%. The glass transition temperature and melting point of PBS are in the range of -24 °C to -37 °C and 110 °C to 147 °C, respectively. In addition, it is quite thermally stable, with an onset decomposition temperature of 353 °C (Gan et al., 2001). PBS is soluble in organic solvents such as chloroform and dichloromethane. It is hydro-biodegradable and begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages, which reduces the polymer molecular weights, allowing for further degradation by many more microorganisms (Aamer et al., 2008). In this era of increasing environmental awareness, PBS is attracting attention as a promising eco-friendly alternative to common plastic because it decomposes naturally into water and carbon dioxide (CO_2). Thus, the scope of its application fields is growing. Up to date, PBS has found applications in agriculture, fishery, forestry, packaging, and other fields in which recovery and recycling of materials after use is problematic. For instance, PBS has been used as packaging materials, dishware, vegetation nets, mulching film, and compost bags. Besides that, this type of polyester has shown considerable promise for uses as bioabsorbable and biocompatible medical materials (Xu and Guo, 2005).

2.3 Polymer Blends

About 30 wt% of the polymer consumptions are comprised of polymer blends nowadays. With the annual growth rate of 9 %, the role of polymer blends becomes very important in various applications. Advantages of polymer blending can be discussed from the perspective of material properties and profits that bring to the manufacturers. There are a number of reasons for blending, which can be divided into two categories, namely material-related and producer-related. The common material-related reasons are shown as follow (Utracki, 1998):

(i) Developing materials with a full set of desired properties.
(ii) Extending engineering resins' performance by diluting them with low-cost commodity polymers.
(iii) Improving a specific property, e.g., ductility, impact strength, barrier property, transparency, abrasion resistance, etc.
(iv) Adjusting the material performance to fit customers' specifications at the lowest price.
(v) Recycling industrial and municipal plastics waste.

The following producer-related reasons are identified:

(i) Better processibility, thus improved product uniformity and scrap reduction.
(ii) Product tailorability to specific customer needs, thus better customer satisfaction.
(iii) Quick formulation changes, thus plant flexibility and high productivity.
(iv) Blending reduces the number of grades that need to be manufactured and stored, thus savings in space and capital investment.
(v) Recyclability of blends achieved by control of morphology, thus improved economy.

According to Kroshwitz (1991), there are two useful types of polymer blends, namely miscible and immiscible. Figure 2.5 shows the morphology of miscible and immiscible blends. The overview of these two types of polymer blends is presented in the following section.

(a) (b)

Figure 2.5 Morphology of a blend of polymer A (solid lines) and polymer B (dashed lines); (a) miscible blend, and (b) immisible blend (Kroshwitz, 1991).

2.3.1 Miscible Blends

Miscibility of polymer blends simply means that there is only one phase present. On the other hand, compatibility refers to the degree of intimacy of a polymer blend, or the capability of the polymer blend components to exhibit interfacial adhesion. It is used to denote a mixture which is homogeneous to the eye, remains homogeneous over the time scale and conditions of use, and has enhanced or desirable properties. The term compatibility has been used often synonymously with miscibility in polymer blends. Following is the distinction made between miscibility and compatibility. Miscibility in polymer blends is neither a requirement nor is it necessarily desirable. However, the interaction of blend components is desirable and the interfacial surface properties and their miscibilities are thermodynamically

interrelated. A binary polymer blend is considered to be miscible if two polymers are able to mix well and dissolve in each other during mixing process to form a single homogeneous phase. In contrast, two polymers, constituting a blend, are compatible if they exhibit two phases on a microscopic level but interact with each other in a manner that provides useful properties and in many cases enhances one or more properties. This implies that there is a degree of compatibility. In many cases, it is desirable to have two phases present since this morphology can improve properties as long as polymer interactions and phase sizes can be controlled. Following are the causes that lead to miscibility of polymer blends (David and Misra, 2001):

(i) Appropriate and intimate mixing that maximizes surface interactions.

(ii) Chemical reactions which result in chemical bond formation.

(iii) Favorable group intermolecular interactions.

(iv) Influence of molecular weight of the species involved.

A miscible blend which consists of only one phase can usually be characterized by a single glass transition temperature (T_g) and homogeneous microstructures with phase size down to 5 – 10 nm (Shonaike and Simon, 1999). Favourable physical and mechanical properties can be derived from the blend of two polymers which are miscible with one another. The properties of the blend are usually between those of its constituents.

Commercially important examples of miscible blends include poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polystyrene (PS), polycarbonate (PC)/2(3)-chloro-1,4-phenylene terephthalate (CPT), poly(vinyl chloride) (PVC)/nitrile rubber, and poly(vinyl chloride) (PVC)/α-methylstyrene-acrylonitrile copolymer (MeSAN)

blends. The glass-transition temperature (Tg) is the primary thermal transition for these blends, and it varies monotonically with composition, following equations such as the Fox equation, as shown in Equation 2.1 (Harper, 2000):

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \qquad (2.1)$$

where Tg_1 and Tg_2 are the glass-transition temperature of the pure component 1 and component 2, respectively, and w_1 and w_2 are the weight fraction of the component 1 and component 2 in the blend, respectively.

On the property-composition diagram in Figure 2.6, the Tg relation usually falls below the tie-line connecting the Tg of the pure components in accordance with the equation, although values above the tie-line have been reported in some noncommercial systems involving very strong intercomponent hydrogen bonds. The glass-transition temperature dependence on composition in this subclass has considerable commercial significance because it largely determines the heat-distortion temperature (HDT) or the maximum-use temperature of the blend (Kroshwitz, 1991).

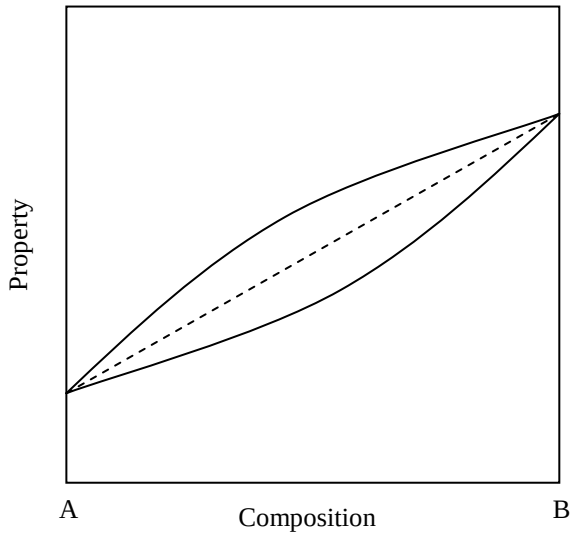


Figure 2.6 Typical property versus composition relations for miscible blends of polymers A and B (Kroshwitz, 1991).

2.3.2 Immiscible Blends

An immiscible blend is defined as a heterogeneous mixture of two or more polymers that are incapable of being mixed and dissolved in each other to form a single homogeneous substance. This type of polymer blend shows discrete polymer phases and multiple glass-transition temperatures corresponding to each component of the blend (Ebewele, 2000). As illustrated in Figure 2.7 (b), the thermal transition behavior of immiscible binary mixtures generally reflects the transitions that occur in each nearly pure amorphous phase present in the system.

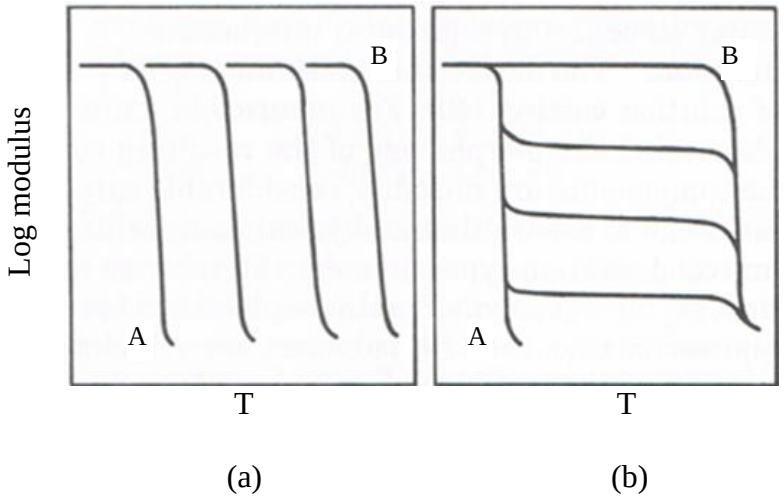


Figure 2.7 Effect of composition on the temperature dependence of the modulus or stiffness of (a) miscible and (b) immisible blends of polymers A and B which are amorphous (Kroshwitz, 1991).

The presence of multiple amorphous phases can result in property versus composition graphs different from those of miscible systems. In immiscible binary mixtures, the major component has a great effect on the final properties of the blend (Harper, 2000), as illustrated in Figure 2.8. This is in contrast with the miscible binary blends that exhibit a more nearly linear composition dependence curve.

A polymer blend with completely immiscible components has limited material utility because the components separate during processing due to poor interfacial adhesion, which is required for optimum and reproducible polymer blend properties. High interfacial tension and disparity between the polarities of these polymer pairs resulting in a sharp interface usually exist between the phases with either very low or no interfacial adhesion. It is believed that this poor interfacial adhesion causes premature failure under stress as a result of the usual crack-opening (Folkes and Hope, 1993).

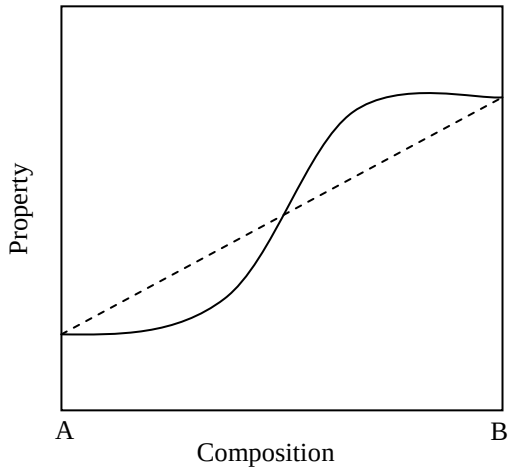


Figure 2.8 Property vs composition profiles of immiscible (solid line) and miscible (dashed line) blends (Harper, 2000).

However, many successful commercial toughened blends such as poly(vinyl chloride) (PVC)/acrylonitrile-butadiene-styrene (ABS) and polycarbonate (PC)/ styrene maleic anhydride (SMA) are either immiscible or partially miscible and consist of two separate *Tg*s and heterogeneous microstructures with dispersed phase size in micrometres as compared to nanometers for the homogenous blends. The overall physicomechanics of these blends depends greatly on the interfacial adhesion across the phase boundaries of the two polymers (Folkes and Hope, 1993).

2.3.3 Compatibilization of Immiscible Blends

In most cases, melt mixing of two polymers results in blends which are weak and brittle, while the low deformation modulus may follow an approximately linear mixing rule, the ultimate properties certainly will not. This is because the incorporation of a dispersed phase in a matrix leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases (Folkes and Hope, 1993). Following is a number of approaches for enhancing the compatibility of a polymer blend.

(1) Achievement of thermodynamic miscibility

In the sense of thermodynamic, miscibility between polymers is determined by a balance of enthalpic and entropic contributions to the free energy of mixing. While for small molecules the entropy is high enough to ensure miscibility, for polymers the entropy is almost zero, causing enthalpy to be decisive in determining miscibility. The change in free energy on mixing (ΔG) is written in Equation 2.2 (Kroshwitz, 1991):

$$\Delta G = \Delta H - T\Delta S \qquad (2.2)$$

where ΔH is enthalpy change, ΔS is entropy change and T is temperature. For spontaneous mixing, ΔG must be negative, and so the subtraction of enthalpy change and entropy change must be negative, as shown in Equation 2.3 (Kroshwitz, 1991):

$$\Delta H - T\Delta S < 0 \qquad (2.3)$$

This implies that exothermic mixtures ($\Delta H < 0$) will mix spontaneously, whereas for endothermic mixtures, miscibility will only occur at high temperatures. The value of

ΔH and ΔS must be determined in order to predict if a mixing occurs spontaneously. The enthalpy change (ΔH) can be evaluated using either the solubility parameter (δ) (cohesive energy density) of the liquids, as presented in Equation 2.4, or the parameter (χ_1) that represents the interaction energy per solvent molecule divided by kT, as shown in Equation 2.5 (Tadmor and Gogos, 2006):

$$\Delta \hat{H} = v_1 \, v_2 \, (\delta_1 - \delta_2)^2 \qquad (2.4)$$

where $\Delta \hat{H}$ is the heat of mixing per unit volume, and v_1 and v_2 are the volume fractions of the solvent and solute.

$$\Delta H = \chi_1 \, kT \, N_1 \, v_2 \qquad (2.5)$$

where k is the Boltzmann constant, T is the temperature of mixing, and N_1 is the number of solvent moles. However, it is difficult to determine which is the solvent and which is the solute in a polymer blend system.

On the other hand, the entropy change can be estimated by applying the Flory-Huggins theory, as expressed in Equation 2.6 (Tadmor and Gogos, 2006):

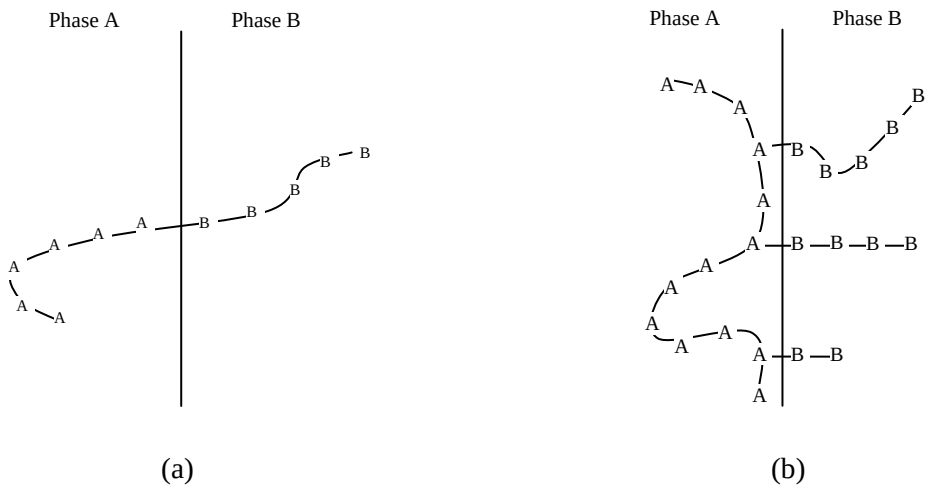
$$\Delta S = -k \, (\, N_1 \ln v_1 + N_2 \ln v_2 \,) \qquad (2.6)$$

Hence, the critical conditions for phase separation can be obtained by using Equation 2.5 and Equation 2.6. Based on the predictions, miscibility of a polymer-solvent system occurs when $| \delta_1 - \delta_2 | < 1.7$, whilst for a polymer-polymer system, miscibility occurs when $| \delta_1 - \delta_2 | < 0.1$ (Tadmor and Gogos, 2006).

(2) Addition of block and graft copolymers

In principle, compatibilizer is a polymer or copolymer that modifies the interfacial character of an immiscible blend and thus improves the compatibility of the blend. It can interact in complex ways to influence final blend properties. One of the effects of compatibilizer is to reduce the interfacial tension in the melt, causing an emulsifying effect and leading to an extremely fine dispersion of one phase in another. Another major effect is to increase the adhesion at phase boundaries, giving improved stress transfer. The third effect is to stabilize the dispersed phase against growth during annealing, again by modifying the phase-boundary interface.

The addition of block or graft copolymers is the most extensively researched approach to the compatibilization of blends. Block copolymers have been more frequently investigated than graft copolymers, and in particular block copolymers containing blocks chemically identical to the blend component polymers. The classical view of how such copolymers locate at interfaces is shown in Figure 2.9.



(a) (b)

Figure 2.9 Penetration of block copolymer or graft copolymer compatibilizers into A and B phases of a polymer blend: (a) block copolymer compatilizer; (b) graft copolymer compatibilizer (Kroshwitz, 1991).

The chemical structure and molecular weight of copolymer have important influences on their effectiveness as compatibilizers. The effect of different copolymer types on the compatibility of polyethylene (PE)/polystyrene (PS) immiscible blend has been studied extensively by Fayt et al. (2000). According to their study, block copolymers were more effective than graft copolymers. Furthermore, diblock copolymers were more effective than triblock or star-shaped copolymers. One of the diblock copolymers used in compatibizing the PE/PS blend is hydrogenated butadiene-styrene diblock copolymer. With only a small amount (less than 2.0 wt%) of the copolymers, a homogeneous and stable phase dispersion of the PE/PS blend was achieved (Fayt et al., 2000).

On the other hand, Paul (1998) suggests that solubilization of a discretely dispersed homopolymer into its corresponding domain of a block copolymer compatibilizer only occurs when the homopolymer molecular weight is equal or less than that of the corresponding block. Nevertheless, stabilization of a matrix homopolymer into its corresponding domain of a block copolymer compatibilizer will occur even if the molecular weights are mismatched. Gaylord (2001) provides the pragmatic view that a balanced molecular weight is needed for copolymer compatibilizers; the segments need to be long enough to anchor to the homopolymer but short enough to minimize the amount of compatibilizer needed, and hence to be cost-effective.

The requirement that the copolymer should locate preferentially at the blend interfaces also has implications for the molecular weight of the compatibilizer. Both the thermodynamic ‘driving force’ to the interface and the kinetic ‘resistive force’ to diffusion increase with molecular weight, suggesting that high molecular weight

copolymers may be used if sufficiently long times are available during the process, but that lower molecular weights must be used if available diffusion times are short.

Furthermore, there are some difficulties of using copolymers with blocks of chemical composition identical to those of the polymer blend components for compatibilization of immiscible blends. One of the difficulties is that the copolymers are often not commercially available. In most cases, the copolymers need to be tailor-made for a particular polymer blend, and this will increase the production time consumed and the overall material cost (Folkes and Hope, 1993).

(3) Addition of functional polymers

Basically, a polymer chemically identical to one of the blend components is modified to contain functional units, which have some affinity for the second blend component; this affinity is usually the ability to chemically react with the second blend component, but other types of interaction such as ionic interaction are possible. The functional modification may be achieved in a reactor or via an extrusion-modification process. Examples include the grafting of maleic anhydride or similar compounds to polyolefins, the resulting pendant carboxyl group having the ability to form a chemical linkage with polyamides via their terminal amino groups. Funtionalized polymers like maleic anhydride or acrylic acid grafted polyolefins are commercially available at reasonable cost to be used as compatibilizers (Folkes and Hope, 1993).

(4) Reactive blending

Reactive blending is a comparatively new approach that relies on the *in situ* formation of copolymers or interacting polymers through covalent or ionic bonding during the melt blending of suitably reactive polymers. The reactive polymers used for compatibilization of immiscible blends are divided into eight categories, with each category having one type of functional group, namely carboxylic acid, hydroxyl groups, maleic anhydride, groups capable of interchange reactions, primary and secondary amines, heterocyclic groups, groups capable of ionic interactions, and others (Baker et al., 2001). Reactive blending differs from other compatibilization methods in which the blend components themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibilizer. The in-situ formed copolymer compatibilizer is located preferentially at the interface where it is most needed, reducing the size of the dispersed, improving the interfacial adhesion between blend phases, and the physical properties of the blends. This route has found commercial application, for instance, in blends of polycarbonate and polyesters, and blends of polyamides with graft-functional polyolefin elastomers. Apart from that, graft-functionalized elastomers produced by melt modification are also commercially available for toughening nylons (Utracki, 1998). Following is a number of reactive blending mechanisms:-

(i) *In situ* Formation of graft or block copolymer by chemical bonding reactions between reactive groups on component polymers; this may also be stimulated by addition of a free radical initiator during blending.

(ii) Formation of a block copolymer by an interchange reaction in the backbone bonds of the components; this is most likely in condensation polymers.